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BETA-SILICON CARBIDE AND ITS POTENTIAL FOR DEVICES

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I INTRODUCTION

Stanford Research Institute has been engaged by the Bureau of Ships to continue studies on preparation of β -silicon carbide for semiconductor device applications. Crystals of silicon carbide are grown from solution, using molten silicon as the solvent.

During earlier periods in the present contract, nitrogen was identified as the dominant donor impurity in the β -silicon carbide crystals grown; these were invariably n-type of low resistivity ($\sim .01$ ohm-cm). Once techniques were perfected for removing nitrogen prior to crystal growth, large increases in resistivity were observed. It then became possible to evaluate the chemical treatment for removing metallic impurities from the starting materials. The improved purity control, obtained during the last report period, resulted in preparation of pure β -silicon carbide crystals having resistivities greater than 100 ohm-cm.

II SUMMARY AND CONCLUSIONS

During this report period, p-type crystals were grown using boron and aluminum additions to the silicon melts. Some difficulty arose as a result of compensation by impurities in the boron employed, but doping levels obtained using aluminum additions appeared quite uniform and amenable to control. Satisfactory results are anticipated for boron when higher purity, zone-refined rod form is used.

Ohmic contacts were obtained on low resistivity (0.1-1.0 ohm-cm) n-type silicon carbide by soldering gold wires directly to the crystals. A number of crystals were prepared for Hall measurements (five-contact method) using this technique.

For high resistivity silicon carbide, ohmic contacts were prepared by flash-fusing carbon-saturated silicon on the crystal surfaces in an arc-image furnace. Rectifying contacts were prepared by this technique using carbon-free silicon of the proper conductivity type.

Hall measurements on recently grown n-type pure crystals of β -silicon carbide indicate room temperature mobilities as high as $4700 \text{ cm}^2/\text{v-sec}$ and carrier concentrations as low as $1.4 \times 10^{15} \text{ electrons/cm}^3$. These results were obtained on relatively low resistivity crystals (0.1-1.0 ohm-cm). Reliable data have not yet been obtained on pure high resistivity crystals or on p-type crystals.

Simple diodes were produced from p-type β -silicon carbide crystals. Intense light was observed at the emitting junction when some of these diodes were being tested.

III EXPERIMENTAL STUDIES AND DISCUSSIONS

A. Crystal Growth

P-type crystals of β -silicon carbide were successfully grown in both boron- and aluminum-doped melts during this quarter. Dopant concentration, crystal type, color, and approximate resistivity for a number of experiments are summarized in Table I.

As low as .005% aluminum in a silicon melt (run 111) produced p-type, ~ 10 ohm-cm crystals containing less than 10 ppm aluminum. During an earlier silicon carbide program, as high as 1% aluminum concentration failed to dope crystals p-type because of the high nitrogen concentration in these crystals. The earlier crystals (run 64), although they contained 250 ppm aluminum, were low resistivity n-type.

Approximately .2% boron added to the melt in run 109 resulted in growth of .5 ohm-cm p-type crystals containing 60 ppm boron. During the earlier program five times as much boron (1%) failed to dope the crystals p-type. The latter crystals (run 60) contained 190 ppm boron, and were high resistivity n-type.

The degree and reproducibility of doping were monitored by emission spectrographic analyses of crystals and silicon melts. The minimum concentration of aluminum in the melt needed to assure the growth of p-type crystals under recently improved purity conditions appears to be approximately .005% aluminum. Less than .005% aluminum in the melt (run 113) yielded n-type high resistivity crystals containing no detectable aluminum.

As yet, the minimum boron concentration in a silicon melt necessary to dope silicon carbide p-type has not been accurately determined. In run 108, powdered Fisher boron failed to dope crystals p-type when added to the melt in concentrations as high as .6%. The powdered boron used in these experiments apparently introduced additional n-type carriers via nitrogen and other impurities. Considerable improvement can be seen from Table I to result from the use of "Knapic grade" boron (run 109). In this case, a 0.21% boron addition to the silicon resulted in

Table I

**DOPANT CONCENTRATION, CRYSTAL TYPE, RESISTIVITY, AND COLOR
IN β -SILICON CARBIDE CRYSTALS**

Run Number	Dopant in Silicon Melt	Dopant in SiC Crystals (ppm)	Crystal Type	Approximate Resistivity (ohm-cm)	Crystal Color
60 ¹	1% Boron ²	190	n	1000	black
61 ¹	.1% Boron ²	30	n	0.1	brown
64 ¹	~ 1% Aluminum	250	n	0.2	green
107	.06% Boron ³	3	n	1000	light green
108	.6% Boron ³	90	most n few p	0.5	dark green
109	.21% Boron ²	60	p	0.5	green
110	~ 4% Aluminum	200	p	low ⁴	blue-green
111	.005% Aluminum	< 10	p	10	yellow-green
113	< .005% Aluminum	none detected	n	very high	yellow

¹Crystals grown during previous program

²"Knapic grade" Boron

³Fisher grade Boron

⁴No usable single crystals

p-type SiC crystals. Analyses of the dopant materials used in these experiments are summarized in Table II. Zone-refined 99.9999% pure boron rod has been obtained, and 99.999% pure aluminum rod has been ordered for use in future experiments. Zone-refined polycrystalline rod should prove easier to degas than the previously used powdered form. If necessary, a separate degassing step will be used to eliminate nitrogen from dopants prior to use in crystal growing runs.

The doping levels obtained using reasonably pure aluminum additions appeared quite uniform and amenable to control. Comparable results are anticipated for boron additions when degassed pure boron is employed as the p-type dopant.

B. Contact and Junction Formation

The formation of good ohmic contacts and rectifying junctions on β -SiC crystals is necessary before meaningful electrical measurements can be obtained.

Two techniques were employed during this period for the formation of reliable contacts. In the case of low resistivity crystals (0.1-1 ohm-cm), ohmic contacts were formed with a thermocompression bonding apparatus using gold wires and an indium-tin solder.

For p-type and high resistivity n-type crystals, contacts were formed by flash-fusing silicon beads in an arc-image furnace. In this process, small bits of silicon are melted on the crystals in the focus of an arc-image furnace apparatus. The crystal rests on a graphite pedestal contained within a glass envelope which is purged with argon gas. The silicon bits on the crystal are heated above 1500°C for approximately five seconds in the focal region of the arc-image furnace.

Ohmic contacts were obtained by fusing carbon-saturated silicon to the silicon carbide crystals. When the silicon was saturated with carbon, ohmic contacts were usually obtained regardless of the carrier type of either the silicon or silicon carbide.

Table II

PURITY OF DOPANT MATERIALS

Metallic Impurities (ppm)*	Fisher Purified Boron Powder	"Knapic Boron" Powder	Hilger Aluminum Turnings
Cu	120	240	24
Ca	350	280	nil
Mg	30,000	90	30
Fe	2,250	900	150
Al	750	100	principal constituent
Sr	15	nil	nil
Mn	640	nil	nil
Ba	10	nil	nil
Pb	1,150	nil	nil

* Semiquantitative emission spectrographic analyses quoted \pm factor of 3

Rectifying contacts were obtained when carbon-free, n-type silicon was fused to p-type SiC crystals or when carbon-free p-type silicon was fused to n-type SiC. It appears that solution and recrystallization of the silicon carbide occurs in this case to provide an SiC-SiC junction. However, no sections have been made yet to establish the nature or depth of the reaction zone. Examination of the region around the contact points under polarized light revealed no strain for properly prepared contacts.

C. Crystal Evaluation

The resistivities of pure (> 10 ohm-cm) and p-type crystals are extremely difficult to measure reliably using a four-point-probe technique owing to contact problems. To obtain the approximate resistivity values reported in Table I, two fused silicon, ohmic contacts were formed on the same face of each crystal. The crystal was then swept with a ten-cycle sine wave and the I-V curve was traced on an oscilloscope.

A modified thermoelectric probe apparatus¹ was used to determine the majority carrier in these crystals. In this procedure, the probes are inserted into liquid gallium or mercury pools contained in parallel grooves machined in a plastic holder. With the grooves placed one millimeter apart, the specimen is positioned to bridge the metallic pools. This method provides a rapid nondestructive means for obtaining good contact when determining the crystal type of small, fragile crystals.

Hall measurements were made on two undoped crystals selected from run 101, using the five-contact technique. The crystals selected had a length-to-width ratio of about 5 to 1. Contacts were made with gold wires using a thermocompression bonding apparatus, in order to obtain accurate positioning of the contact points. This necessitated the use of relatively low resistivity n-type crystals in order to form reliable, ohmic contacts. While the flash-fusion method would permit preparation

¹Gould, H. J., Determining p- and n-Type Conduction in Very Small Crystals, Rev. Sci. Instr. 33, No. 12 (1962)

of ohmic contacts on high resistivity or p-type crystals, we have not yet developed techniques for forming five, closely positioned contacts in this manner.

Values obtained from measurements made at Stanford Research Institute and at Hewlett-Packard Associates are shown in Table III.

Table III

RESULTS OF HALL MEASUREMENTS ON β -SiC CRYSTALS

Crystal Number Measuring Laboratory	101 H SRI	101 H HPA	101 A SRI
Hall Constant $\left(\frac{\text{cm}^3}{\text{coul}}\right)$	443	624	5330
Carrier Concentration (cm^{-3})	1.67×10^{16}	1.18×10^{16}	1.38×10^{15}
Carrier Mobility $\left(\frac{\text{cm}^2}{\text{v-sec}}\right)$	2100	3265	4670
Crystal Resistivity (ohm-cm)	0.179	0.163	0.971

Of particular interest in these measurements are the high mobility values observed as compared with values reported in the literature for pure α -SiC ($\sim 100 \text{ cm}^2/\text{v-sec}$) and the values obtained for impure β -SiC ($10\text{-}30 \text{ cm}^2/\text{v-sec}$).^{2,3} While these values are somewhat surprising, it is not unreasonable to expect large differences between the α and β modifications. Although data must be obtained on more crystals to confirm these results, the reproducibility of measurements taken in two laboratories is encouraging.

In calculating the carrier concentration, the factor $\frac{3\pi}{8}$ was employed. While this factor may contribute some error to the calculations, the error

²Pohl, R. G., Electrical Properties of Beta Silicon Carbide, Silicon Carbide, A High Temperature Semiconductor, Pergamon Press, 1960, p. 319

³Halden, F. A., W. P. Meuli, W. J. Fredericks, Growth of Silicon Carbide Single Crystals, Stanford Research Institute Final Report, Bureau of Ships, Contract No. NObsr-72772 (1961)

would probably not exceed a factor of two. In the event that the maximum and minimum of the energy in the valence and conduction bands, respectively, are displaced, this factor should be quite good. Some indications that this is the case are presented in the following section, and also in the literature.⁴

D. Device Fabrication Studies

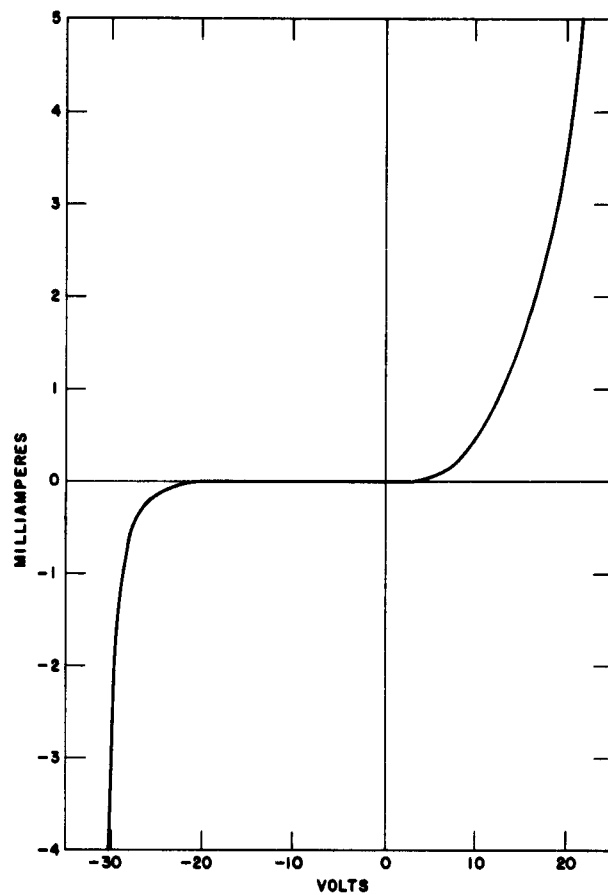
Simple diodes were fabricated during this period by fusing two dots of silicon to the same face of a p-type SiC crystal (10 ohm-cm). One dot was n-type, carbon-free silicon (rectifying junction), and the other was p-type, carbon-saturated silicon (ohmic contact).

The I-V characteristic for one of the p-n junctions studied is shown in Fig. 1. The data were obtained by sweeping the diode with a ten-cycle sine wave and observing the I-V characteristic on an oscilloscope. It will be noticed that the breakdown is relatively sharp, but most of the samples tested showed a soft breakdown starting around 15 volts. The voltage drop in the forward direction is appreciable, probably because of the high series resistance of the thin, narrow, high resistivity crystals used with contacts 5 to 10 mils apart.

Due to high series resistance and small crystal volume, appreciable heating took place when the current was increased. This affected the I-V characteristic of the p-n junction by greatly lowering the forward voltage drop. In addition, the breakdown sharpened, but the breakdown voltage remained almost constant. A possible explanation for this is that the impurity levels are far above the valence band, so the impurities are effectively ionized at high temperatures. For α -SiC the level of aluminum has been determined to be 0.275 ev above the valence band.

By passing the maximum power available through this crystal, it was heated resistively until the quartz support on which it was mounted began to soften (1300°-1400°C). Upon cooling to room temperature, the diode again retraced exactly the curve shown in Fig. 1.

⁴Keyes, R. W., Review of Section IV, Silicon Carbide, A High Temperature Semiconductor, Pergamon Press, 1960, p. 395



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FIG. 1 β - SILICON CARBIDE DIODE I-V CHARACTERISTICS

A noticeable amount of orange light was radiated from the emitting junction when the diode was forward biased. At 3 ma, corresponding to a current density of 50 amp/cm^2 , the light was easily observable with the naked eye even when a microscope light was shining on the diode. As the current density was increased, the intensity of the emitted light rose and the wave length decreased. At about one amp the color of the light was green.

With a reduced series resistance, the p-n junction may have possibilities as a small light source. Similar observations have been made for α -SiC where the radiant light was yellow at low current densities and changed to blue for large current densities. The light emission has been explained to be due to recombination of the injected carriers with the carriers of the SiC. At low current densities the recombination takes place via impurity levels or traps in the band gap. As the current is increased and the impurity levels or traps become filled, the chances for direct recombination across the energy gap rise. At very high current density most of the light comes from direct recombination, and the color of the light is thus proportional to the energy band gap. The above observations may indicate that the band gap for β -SiC is slightly smaller than the band gap for α -SiC. If the wave length for the green emitted light is taken to be 0.52μ , the equivalent band gap is approximately 2.4 ev. This is in close agreement with energy gaps reported in the literature for β -SiC.⁴

During the experiment at high current densities, it was noticed that the highest temperature was reached directly under the light-emitting portion of the diode. This indicates emission of phonons in the recombination process and thus that the maximum and minimum of the energy in the valence and conduction bands, respectively, are displaced.

IV FUTURE WORK

During the next quarter doping levels necessary to prepare p-type crystals will be correlated with electrical measurements on these crystals. Attempts will be made to form sharp p-n junctions during crystal growth by rapid addition of boron or aluminum to the melt when the crystals are approximately 1/2 to 2/3 grown. Additional crystal growth during the remainder of the run should then be p-type. Grown junctions will be evaluated, and specific β -silicon carbide devices will be fabricated as time permits.

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